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(57) Abstract

Fibre or film having a matrix of a copolymer from 50 to 95 % by weight ethylenically unsaturated carboxylic monomer and 5 to 50 % by weight copolymerisable ethylenically unsaturated monomer is characterised in that the matrix contains a dissolved chemical which alters the properties of or has an effect on the fibre or film or on an aqueous fluid absorbed by the fibre or film. The chemical can for example be an antibacterial agent or an acidic reagent capable of reacting with ammonia to reduce the ammoniacal smell of urine. The fibre or film can be used to apply a controlled quantity of a chemical to a desired location.

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Fibre and Film

Technical Field

This invention relates to fibre and film and has particular but not exclusive reference to fibre and film of water-absorbent water-insoluble material. Water-absorbent water-insoluble materials are of use in many absorbent products, particularly products for absorbing aqueous body fluids such as baby diapers, incontinence pads, sanitary napkins and tampons, and in wiping materials for mopping up spills of aqueous fluids. Most water-absorbent water-insoluble materials are available only in powder form. There are problems in retaining an absorbent powder in the desired position in the absorbent product, for example in diapers. Fibre, whether staple fibre or continuous filaments, can be more effectively retained in position by incorporation in a fabric, and fibre or film can also be effectively retained in position in other products.

Background Art

EP-A-268498 describes a water-absorbent water-insoluble polymeric fibre, film, coating, bonding layer or foam, made by forming a substantially linear polymer of water-soluble ethylenically unsaturated monomer blends comprising carboxylic and hydroxylic monomers and then reacting the carboxylic and hydroxylic monomers in the linear polymer to form internal crosslinks within the polymer.

EP-A-269393 describes a water-absorbent water-insoluble crosslinked polymer fibre or film made by dry extrusion of a solution of a substantially linear polymer formed from a water-soluble blend of monoethylenically unsaturated monomers comprising a plasticising monomer and evaporation of the solvent. The fibre or film is further plasticised, stretched

and then crosslinked.

EP-A-342919 describes film or fibre made by extrusion and stretching from a polymer of water-soluble ethylenically unsaturated monomers that include ionic monomer. A counterionic lubricant compound is absorbed into the surface of the fibre or film before or during the stretching.

EP-A-397410 describes a water-soluble linear polymer of carboxylic acid monomers such as acrylic acid and a hydroxylic monomer which can be crosslinked, after being shaped by extrusion of an aqueous solution of the polymer as fibres or film, to form crosslinks between the carboxyl and hydroxyl groups.

Disclosure of Invention

According to the present invention fibre or film has a matrix of a copolymer formed from 50 to 95% by weight ethylenically unsaturated carboxylic monomer and 5 to 50% by weight copolymerisable ethylenically unsaturated monomer, and it is characterised in that the matrix contains a dissolved chemical which alters the properties of or has an effect on the fibre or film or on an aqueous fluid absorbed by the fibre or film.

The fibre or film is preferably water-absorbent fibre or film in which the matrix copolymer is sufficiently crosslinked that it is water-insoluble. The fibre or film can alternatively be non-crosslinked water-soluble fibre or film which is used as a means of applying a controlled quantity of the dissolved chemical to a desired location, or it can be fibre or film which is partially crosslinked or lightly crosslinked, that is to say having some linking of polymer chains to increase the molecular weight of the polymer but not sufficient crosslinking to cause the fibre or film to be water-

insoluble. Such light or partial crosslinking can control the rate at which the fibre or film dissolves in water or other aqueous fluids and hence the rate at which the dissolved chemical is released.

The dissolved chemical may be an element or a chemical compound which may for example be a water-soluble inorganic salt or a non-volatile water-soluble organic compound. The dissolved chemical need not be water-soluble, provided that it can be dissolved in the solution of the non-crosslinked matrix copolymer. The presence of the copolymer may promote the solubility of some organic compounds in aqueous solutions containing it. The chemical can initially be dissolved in an aqueous solution of high or low pH provided that it remains in solution in the aqueous copolymer solution. The dissolved chemical can for example be a carboxylic acid or a salt or ester thereof, a sulphonic acid or a salt or ester thereof, an alcohol, a quaternary ammonium salt, an amine or a salt thereof.

The dissolved chemical may be released into aqueous fluid absorbed into the fibre or film and may for example alter the pH of the fluid, react with a chemical present in the fluid or kill or inhibit the growth of microorganisms in the fluid.

The fibre or film may be formed by extruding a solution, particularly an aqueous solution, of the matrix copolymer in its non-crosslinked state containing the dissolved chemical into a gaseous environment adapted to remove the solvent to form the fibre or film. The matrix copolymer can subsequently be crosslinked if required. The fibre or film may be stretched subsequent to formation, preferably before the crosslinking system is activated.

The invention also includes a process for applying a controlled quantity of a chemical to a desired location,

characterised in that a solution of the said chemical and a non-crosslinked polymer of 50 to 95% by weight ethylenically unsaturated carboxylic monomer and 5 to 50% by weight copolymerisable ethylenically unsaturated monomer is extruded through a spinneret or die into a gaseous environment wherein solvent is removed to form fibre or film, and the fibre or film is applied to the desired location, optionally after crosslinking.

Preferably, the non-crosslinked matrix copolymer is substantially linear. It is formed from a blend of ethylenically unsaturated monomers. The monomers are preferably selected so that the blend is water-soluble and so that a crosslinked polymer can be formed which is water-absorbent. Ways of selecting monomers for this purpose are known for example from EP-A-397410 mentioned above. Generally, the blend of ethylenically unsaturated monomers is an anionic blend and usually comprises a carboxylic acid monomer, preferably with a non-ionic monomer. The monomers used in the invention may be allylic but are usually vinylic, most preferably acrylic, monomers.

Preferred carboxylic monomers are methacrylic acid or acrylic acid, but maleic acid or anhydride, itaconic acid or any of the other conventional ethylenically unsaturated carboxylic acids or anhydrides are also suitable. The copolymer can optionally additionally contain monomer units derived from an ethylenically unsaturated sulphonic acid such as 2-acrylamido-2-methyl-propane sulphonic acid or allyl sulphonic acid. Carboxylic and sulphonic monomer units may be present in the final copolymer in free acid or water-soluble salt form, suitable salts being formed with ammonia, an amine or an alkali metal. The proportion of salt and free acid groups can be adjusted after formation of the crosslinked copolymer or after polymerisation of the linear copolymer or before polymerisation. Generally, the molar ratio of free

carboxylic acid groups to alkali metal or other salt carboxylic acid groups in the final copolymer (and often also in the monomers that are used to form the linear copolymer) is from 1:1 to 1:10. The ratio is usually at least 1:2 and often at least 1:3. It is usually below 1:6 and often below 1:5.

When a crosslinking reaction involving reaction with the carboxylic acid groups is used it is usually preferred that at least some of the carboxylic acid groups should be present as free acid groups before the crosslinking occurs. For instance, for this purpose, it may be adequate for 10 to 75%, preferably 25 to 75%, of the acid groups to be in free acid form before the crosslinking occurs.

Although the linear copolymer is generally made by polymerisation of carboxylic acid monomer (in free acid or salt form), it is also possible to make the copolymer by polymerisation of monomer that can be subsequently reacted to form the carboxylic acid copolymer. For instance, the carboxylic acid groups that are to be present (in free acid or salt form) in the fibre or film may be present initially in the linear copolymer in the form of hydrolysable ester groups, such as methyl ester groups, that can then be hydrolysed while in the form of a linear copolymer to yield carboxylic acid (free acid or salt) groups.

The copolymerisable ethylenically unsaturated monomer for the matrix copolymer may be a water-soluble ethylenically unsaturated monomer such as acrylamide or may be a water-insoluble monomer, for example an olefin, such as isobutylene, an aromatic ethylenically unsaturated monomer, such as styrene or a substituted styrene, an alkyl ester of acrylic or methacrylic acid, such as methyl or ethyl acrylate or methacrylate, butyl acrylate or methacrylate or 2-ethylhexyl acrylate or methacrylate, vinyl acetate or acrylonitrile. One or more copolymerisable monomers may be present. A monomer

that will provide groups for internal crosslinking with the carboxylic groups (as discussed below) is usually included. Other non-ionic monomers that may be used include ethylenically unsaturated monomers that carry a pendent group of the formula $-A_mB_nA_pR$, where B is ethyleneoxy, n is an integer of at least 2, A is propyleneoxy or butyleneoxy, m and p are each an integer less than n and preferably below 2 and most preferably zero, and R is a hydrophobic group containing at least 8 carbon atoms, as described in more detail in EP-A-213799. The comonomer(s) are generally present in amounts of at least 5% and preferably at least 10% by weight based on the monomers used for forming the copolymer, and they may be present in amounts up to about 50%, generally below 45%, by weight.

The substantially linear copolymer may be formed from the monomer blend in any conventional manner. It may be preformed and then dissolved to form a copolymer solution. For instance, it may be made by reverse phase polymerisation if the monomer blend is soluble in water or by water-in-oil emulsion polymerisation if the blend is insoluble in water, eg at a low pH. However, this can incur the risk that the copolymer may be contaminated by surfactant and this is undesirable. Preferably, therefore, the copolymer is made by aqueous solution polymerisation or other solution polymerisation methods. It may be dried before further processing, but preferably not. Generally, it is formed by solution polymerisation in the solvent in which it is to be extruded (usually water).

The polymerisation can be conducted in conventional manner in the presence of conventional initiators and/or chain transfer agents to give the desired molecular weight.

The concentration of copolymer in the solution to be extruded is generally in the range 5 to 50% and will be selected, having regard to the molecular weight of the

copolymer, so as to give a solution having a viscosity that is convenient for extrusion. The solution can be extruded through a spinneret, suitably one of the type conventionally used in synthetic fibre production. The concentration of copolymer is usually at least 15% by weight, with values of 30% to 45%, eg 35% to 40%, by weight often being particularly suitable.

The solution that is extruded may have a viscosity as low as, for instance, 20,000mPa.s at 20°C but generally the viscosity is at least 70,000 and usually at least 100,000 and sometimes at least 120,000mPa.s. It can be up to 150,000 or even 200,000mPa.s. Higher values are generally unnecessary. All these viscosities are measured at 20°C using a Brookfield RVT spindle 7 at 20rpm. The viscosity desirably is also relatively high at the extrusion (spinning) temperature, which typically is elevated, for instance above 80°C but below the boiling point of the copolymer solution. Preferably, the solution at 80°C has a viscosity of at least 5000 or 10,000mPa.s and most preferably at least 20,000mPa.s. For instance, it may be in the range 50,000 to 100,000mPa.s. These values may be obtained by extrapolation from values obtained using a Brookfield RVT viscometer spindle 7 at 20rpm at a range of temperatures somewhat below 80°C.

The molecular weight of the linear copolymer that is extruded may be as low as, for instance, 50,000 or 100,000 but preferably is above 300,000 and most preferably is above 500,000. For instance, it may be up to 1 million or higher.

The solvent of the solution that is extruded is usually water but can be methanol or other suitable organic solvent or may be a blend of water and organic solvent. The solvent must be volatile so as to permit rapid evaporation after extrusion. The gaseous environment into which the solution is extruded is preferably hot air. When forming fibre, the hot air or other gas can be contained in a cell of the type conventionally used

for dry spinning, or flash spinning can be used. The spun filaments can be taken up on conventional textile machinery such as a godet, as a yarn or tow. A conventional spin finish is usually applied to the fibre before it is taken up.

When forming film, the solution can for example be extruded via a slit die or an annular die through a heated gaseous environment, generally hot air, on to a support surface, for example a heated rotary drum. The support surface has release properties. Drying of the film continues on the drum, and the film is stripped from the drum and taken up on rolls. The moisture content of the film as it is taken up is generally in the range 8 to 25% based on the dry weight of film, most preferably 10 to 20%.

It is preferred to stretch the fibre or film before it is collected. Stretching is effected by having the speed of the collection apparatus, for example the take-off godet, higher than the extrusion rate of the polymer solution (the linear velocity of the polymer solution through the exit capillary of the spinneret or die). The ratio of the take-off speed to the extrusion speed is generally up to 10:1 but is preferably in the range 2-8:1, most preferably 3-6:1.

The diameter of the final fibre preferably corresponds to a weight of below 20 decitex per filament, for example in the range 2 to 15 decitex per filament. This is the decitex after stretching; if stretching is used, the decitex per filament after initial extrusion may be higher than the range quoted above. If stretching is used it is carried out before crosslinking.

If the linear copolymer is to be crosslinked, it is crosslinked after extrusion. The crosslinking can be effected by reaction into the backbone of the linear copolymer but preferably is by crosslinking through pendent groups provided

by one or more monomers that have been polymerised to form the linear copolymer. The crosslinking can be ionic, for instance as a result of exposing the linear copolymer to any of the known ionic crosslinking agents, preferably polyvalent metal compounds such as polyvalent aluminium compounds, for example aluminium sulphate. Organic compounds may be used instead of inorganic compounds to provide the crosslinking.

Preferably, however, the crosslinking is covalent between pendent groups in the linear copolymer. The covalent crosslinking generally arises as a result of the formation of ester, amide (or imide) or urethane groups by reaction with carboxylic acid groups after extruding the copolymer. Ester groups are preferred.

The crosslinking reaction may be with an external crosslinking agent. Various systems for externally crosslinking the copolymer are described in EP-A-269393 and these can be used in the present invention. For example, the carboxyl-functional linear copolymer can be crosslinked by a diisocyanate to form urethane crosslinks or by a polyamine such as ethylene diamine to form amide crosslinks or by a polyfunctional reagent containing hydroxyl and/or epoxide groups to form ester crosslinks. Preferably, however, the polymer is internally crosslinked by reaction between reactive groups within the extruded copolymer. Usually the carboxylic groups act as one type of reactive group and are reactive with hydroxyl, epoxide, amino or blocked isocyanate groups. Particularly preferred systems are described in detail in EP-A-268498. In these systems the extruded copolymer is formed from a monomer blend comprising monomer that provides carboxylic acid monomer groups and monomer that provides hydroxyl or epoxide groups that can react with the carboxylic acid groups to form ester crosslinks that contain only carbon and oxygen atoms in the linkages, and these carboxylic and hydroxyl or epoxide groups are reacted after extrusion to form the said

crosslinks. Generally, the carboxylic acid groups are provided by acrylic acid or methacrylic acid and the hydroxyl groups are provided by allyl alcohol, an epoxide-substituted vinyl monomer such as glycidyl methacrylate or a hydroxyalkyl ester of a vinyl carboxylic acid such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate or 3-hydroxypropyl methacrylate or by vinyl alcohol groups. Alternative hydroxyl group-containing monomers are those of the formula $CHR^1=CR^2-Y-M_a-OH$, where R^1 is hydrogen or carboxy, R^2 is hydrogen or methyl, Y is O, CH_2O or COO, M is alkyleneoxy, for example ethyleneoxy or 1,2-propyleneoxy, and a is an integer greater than 1 and preferably at least 5, as disclosed in EP-A-397410. Alternatively, the comonomer can contain a primary or secondary amine group, for example 2-aminoethyl methacrylate, which reacts to form amide crosslinks, or it can contain an isocyanate group (which may need to be blocked to prevent crosslinking during extrusion), for example 2-isocyanatoethyl methacrylate, to form urethane crosslinks.

Reference should be made to EP-A-269393, EP-A-268498 and EP-A-397410 for a full disclosure of suitable materials and methods of extrusion and of crosslinking that can be used in the present invention. As stated above, heat-activated crosslinking is preferred. The temperature used to crosslink the fibre or film can for example be in the range 150 to 250°C, with the temperatures during extrusion and stretching being lower than the crosslinking temperature, preferably at least 30°C lower.

Prior to extrusion, it is necessary to produce a homogeneous solution of the chemical and the copolymer in water. This can be achieved by directly dissolving the chemical into the copolymer solution or, preferably, by mixing an aqueous solution of the chemical with the copolymer solution. The mixing of the solutions can be carried out using standard mixing techniques such as high-shear or low-shear

mixing, ultrasonically or by pumping the mixture through a static mixer. Mixing can be carried out by injection of the chemical or a solution of the chemical into the copolymer solution in the extruder as it passes to the spinneret or die. The chemical and the copolymer solution can be mixed by an in-line dynamic or static mixer positioned downstream of the point of injection.

The copolymer solution containing the dissolved chemical is capable of being converted into a variety of shaped forms such as fibre (including filaments, fibrils and pulp) and film (including sheet and coatings) with evaporation of the solvent after shaping. Fibre produced can be further processed into milled fibres, chopped fibres, yarns, webs or woven, knitted or nonwoven fabrics.

The dissolved chemical should not be a chemical which causes precipitation of the copolymer from aqueous solution. In most cases the chemical is substantially non-reactive with the copolymer. It is preferred in any case that the chemical does not react or cause crosslinking of the copolymer or form a covalent bond to the copolymer at spinning temperatures, that is at temperatures up to 100°C. Reaction to form an ionic or coordinate bond, for example reaction with the carboxylic acid groups to form a salt or complex, can generally be tolerated provided that the reaction does not crosslink the copolymer at temperatures up to 100°C. Reaction with the copolymer at crosslinking temperatures is in general acceptable.

The fibre or film can for example comprise a crosslinked copolymer matrix containing a dissolved chemical which is not bonded to the copolymer. Such a crosslinked fibre or film is generally water-insoluble and water-absorbent, and the chemical is capable of being leached from the fibre or film by aqueous fluid contacting the fibre or film. The chemical can thereby impart its desired properties to the aqueous fluid or to a film

or fabric or bundle of fibre containing absorbed aqueous fluid.

The chemical may form a salt with the copolymer; this will usually reduce the rate at which the chemical is leached into aqueous fluid but will not prevent leaching. Alternativaly, the dissolved chemical can be more strongly bonded to the copolymer. The fibre or film can be heated to bond the chemical to the copolymer; the heat used in crosslinking may for example cause such bonding. A strong bond such as a covalent bond may prevent leaching of the chemical from the fibre or film so that the chemical is fixed on the fibre or film and will continue to react in the desired way with aqueous fluid coming into contact with the fibre or film. Any reaction taking place between the dissolved chemical and the fibre or film should not be such as to use up the functional groups of the dissolved chemical which are responsible for its desirable chemical properties in use. The dissolved chemical should be substantially non-volatile at crosslinking temperatures to avoid loss of chemical.

Alternatively, the fibre or film can comprise a non-crosslinked, partially crosslinked or lightly crosslinked copolymer matrix containing the dissolved chemical. A partially crosslinked copolymer can for example be formed by using a lower temperature and/or a shorter time in the crosslinking step. For example, when ester crosslinking between carboxylic acid and alcohol groups is used, the temperature of crosslinking can be for example 130 to 200°C and the time for which the fibre or film is treated can for example be half or less than half of the time used to form water-insoluble crosslinked fibre or film. Partially crosslinked or even non-crosslinked fibre or film can thus be formed from the same copolymer solution as water-insoluble crosslinked fibre or film. Lightly crosslinked copolymer fibre or film can be formed by using a low proportion of crosslinking agent or crosslink-forming comonomer so that the degree of crosslinking

is not sufficient to cause insolubility in water. The non-crosslinked, partially crosslinked or lightly crosslinked copolymer is water-soluble, although a partially crosslinked or lightly crosslinked copolymer will generally have a lower rate of dissolution in aqueous fluids than a non-crosslinked copolymer. A web, for example a woven, knitted or non-woven fabric, of non-crosslinked, partially crosslinked or lightly crosslinked fibre can be used as a way of presenting a water-soluble chemical in a particular use. The web can for example be used for topical application of a therapeutical chemical to a part of the body where it will contact aqueous body fluids so that the dissolved chemical is released into the aqueous body fluids. A web of water-insoluble water-absorbent fibre having a matrix of crosslinked copolymer and containing a dissolved therapeutical chemical can also be used for this purpose if it is preferred to avoid dissolution of the fibre matrix.

The dissolved chemical can for example be an acidic reagent capable of reacting with ammonia to reduce the ammoniacal smell of urine. The dissolved chemical can be an antiseptic material such as an antibacterial agent, for example chlorocresol. The dissolved chemical can alternatively be a water-soluble dye, for example an acidic or basic dye, or optical brightener, which may or may not chemically react with the copolymer to become fixed to the fibre or film.

The proportion of dissolved chemical in the fibre or film is generally up to 20% by weight, for example up to 15%, preferably up to 10%, by weight, based on the copolymer. Usually, the proportion of dissolved chemical is at least 0.02%, preferably at least 0.1%, by weight to achieve a significant effect. For acidic agents used to counteract ammoniacal odour the proportion of dissolved chemical is generally up to 5% by weight, and preferably at least 1%. Bactericidal agents when used preferably comprise at least 0.1% by weight of the fibre or film and usually no more than 1%.

Dyes and optical brightening agents are usually used in amounts of at least 0.05% by weight of the fibre or film, for example up to 0.5%.

The water-absorbent water-insoluble fibre or film of the present invention can be used in various products. It can, for example, be used in absorbent personal products such as tampons, disposable diapers, sanitary napkins or incontinence pads. The absorbent fibre is preferably used in combination with other fibres, for example cellulosic fibres such as cotton or regenerated cellulose fibres, including multi-limbed cellulose fibres as described in EP-A-301874, or polypropylene or polyester fibres. The absorbent fibres can be intimately mixed with said other fibres, for example by carding or air-laying the fibres together to form a web of mixed fibres. Alternatively, the absorbent fibre or film can be used as a layer, for example a non-woven fabric of absorbent fibre, sandwiched between layers of other fibres. The proportion of absorbent fibre in a blend with cellulosic fibres for absorbent products can for example be at least 5% and up to 95%, preferably at least 10% and up to 50%, by weight. The absorbent fibre can also be used at similar levels in conjunction with fluffed wood pulp or synthetic fibre pulp, for example polyolefin pulp, in absorbent products.

A yarn, woven fabric or nonwoven fabric comprising the absorbent fibre can be used as a swellable material which prevents ingress of water in underground cables. A yarn or fabric tape or an absorbent film can be used to wrap cable or can be laid longitudinally in the cable.

The absorbent fibre or film can be used in many other applications of the types described in Research Disclosure, January 1992 at pages 60-61, for example in filters, absorbent liners or mats for packaging, disposable wipes, mats, shoe insoles or bed sheets, swellable gaskets or seals, moisture

retention mats in horticulture, and moisture- retaining packaging or swellable self-sealing stitching threads.

The invention is illustrated by the following Examples. In the Examples, various test results on absorbency are quoted. The absorbency can be measured by the free swell test, in which 0.5g fibre is dispersed in 30 ml aqueous liquid and left for 5 minutes. The aqueous liquid used is generally 0.9% by weight saline solution, which is generally absorbed to a similar extent to body fluids such as urine. The test can alternatively be carried out with either tap water or demineralised water, but results quoted below are for 0.9% saline solution. For all absorbency measurements, the fibre is conditioned at 65% relative humidity and 20°C before being tested. The dispersion is then filtered through a sintered Mark 1 funnel of pore size 100-160 microns and is left for 5 minutes or until it stops dripping. The weight of the water filtered through the funnel is weighed and the weight of water absorbed by the fibre is calculated by subtraction.

In an addition to the above test, the retention by the fibre of the aqueous liquid such as saline solution after application of pressure is measured by weighing the water expressed after application of pressure at about 3.4 KPa for 5 minutes or until dripping stops.

In a further test of absorption, the absorbency under load is measured by maintaining the fibre in contact with a 0.9% by weight saline solution for an hour while applying a load of 1.7KPa.

Example 1

32.1 g citric acid was dissolved in 50 g water. This solution was added to 4.5 kg of a 38% by weight aqueous solution of a copolymer of 78 mole % acrylic acid (75%

neutralised as sodium salt), 20 mole % methyl acrylate and 2 mole % hexapropylene glycol monomethacrylate. The solution was added at 55 to 65°C and stirred with a paddle stirrer for 2 hours to produce a spinning solution containing about 2% by weight citric acid based on copolymer.

This solution was spun into fibre through a spinneret into a cell where water was evaporated from the fibre. The temperature of the dispersion at the spinneret was between 90 and 100°C. The cell was heated by tube wall heaters at 150°C. The filaments were of approximately 15dtex. Staple fibre samples of the resulting multifilament tow were crosslinked by heating in air at 160°C for 90 minutes. The free swell absorbency, retention and absorbency under load of the resulting fibre were measured in each case by the methods described above. The results obtained were:

Free Swell g/g	Retention g/g	Absorbency under load g/g
56.8	52.1	6.4

The fibre was compared in a simple smell comparison test with a similar fibre containing no citric acid. A solution of ammonium hydroxide was added to a known weight of each fibre until the ammonia odour was judged to be of the same strength. The citric acid fibre showed a slight advantage, that is it required more ammonia to give the same odour strength.

Example 2

Staple fibre samples of the spun filaments of Example 1 were partially crosslinked by heating in air at 160°C for 60 minutes. The free swell absorbency of the fibre could be measured as 57.5 g/g. The absorbency under load of the fibre could not be measured because the test requires that the fibre is kept in contact with an aqueous saline solution for an hour, and the fibre dissolved during this time. The fibre was

ultimately soluble in aqueous fluids such as 0.9% saline solution but had a slower rate of dissolution than non-crosslinked fibre.

The fibre had a similar performance to the fibre of Example 1 in an ammonia smell comparison test.

Example 3

9.91 g chlorocresol antibacterial agent was dissolved in 30.6 g 1N sodium hydroxide solution. This solution was added to the copolymer solution described in Example 1 at 65°C and stirred for 2 hours with a paddle stirrer to produce a spinning dope of increased viscosity. Fibre spun from the dope was crosslinked at 160°C for 60 minutes and had a free swell absorbency of 54.6 g/g and a retention of 53.6 g/g. Both the swollen gel formed from the fibre in the absorbency tests and the saline extract which had been in contact with it were found to contain chlorocresol, indicating that the chlorocresol antibacterial agent is released from the fibre into aqueous media.

The non-crosslinked fibre containing chlorocresol, which substantially dissolves in the free swell absorbency test, can also be used for topical application of the antibacterial agent.

Example 4

Astrazon Blue 5 GL liquid basic dye was added to the copolymer solution of Example 1 by stirring in a beaker at 30-40°C to give a solution containing approximately 0.1% dye by weight on polymer. The resulting dope was spun into fibre as described in Example 1. The fibre was crosslinked at 160°C for 90 minutes. Test results are given below. The dye did not leach from the crosslinked gels during absorbency testing,

indicating that it became chemically bound to the polymer. No dye degradation was apparent from the above treatment.

Test Results:-

Free swell 52.3g/g
Retention 51g/g
Absorbency under load 8.6 g/g.

Example 5

Nylosan (Registered Trade Mark) red acidic dye was added to the copolymer solution of Example 1 by stirring in a beaker at 30-40°C to give a solution containing 0.19% dye by weight on polymer. Fibre was produced as described in Example 1 and crosslinked at 160°C. No dye degradation was apparent, nor did the dope suffer from the additive. The dye did not leach out when the polymer was swollen.

Example 6

A solution of the optical brightening agent, Blankophor ANR, was mixed with the copolymer solution of Example 1 in a beaker at 30-40°C such that the resulting spinning dope had 0.1% of the optical brightening agent by weight on polymer. Fibre was spun as described in Example 1 and crosslinked for 11 minutes at 200°C. No deterioration of the dope was observed. The absorbency results were as follows:

Free Swell 35.8g/g
Retention 34.8g/g.
Absorbency under load 7.2g/g.

The swollen gel and the saline extract after absorbency testing fluoresced under UV light, indicating that the optical brightening agent had not been immobilised in the polymer matrix.

CLAIMS

1. Fibre or film having a matrix of a copolymer formed from 50 to 95% by weight ethylenically unsaturated carboxylic monomer and 5 to 50% by weight copolymerisable ethylenically unsaturated monomer, characterised in that the matrix contains a dissolved chemical which alters the properties of or has an effect on the fibre or film or on an aqueous fluid absorbed by the fibre or film.

2. Fibre or film according to claim 1, characterised in that the matrix copolymer is sufficiently crosslinked that the fibre or film is water-absorbent and water-insoluble.

3. Fibre or film according to claim 1, characterised in that the copolymer is partially crosslinked or lightly crosslinked but is not sufficiently crosslinked that the fibre or film is water-insoluble.

4. Fibre or film according to claim 2, characterised in that the dissolved chemical is an acidic reagent capable of reacting with ammonia to reduce the ammoniacal smell of urine.

5. Fibre or film according to any of claims 1 to 3, characterised in that the dissolved chemical is an antibacterial agent.

6. Fibre or film according to any of claims 1 to 3, characterised in that the dissolved chemical is a dye or optical brightener.

7. Fibre or film according to any of claims 1 to 6, characterised in that the proportion of dissolved chemical in the fibre or film is 0.02 to 20% by weight.

8. Fibre or film according to any of claims 2 to 7,

characterised in that the matrix copolymer is crosslinked by ester crosslinks.

9. Fibre or film according to claim 8, characterised in that the copolymerisable ethylenically unsaturated monomer consists at least partly of a hydroxyl-functional or epoxide-functional comonomer, and that the ester crosslinks are formed by reaction between carboxylic acid groups derived from the carboxylic monomer and hydroxyl or epoxide groups derived from the copolymerisable monomer.

10. A process for the production of fibre or film by extruding a solution of a matrix copolymer formed from 50 to 95% by weight ethylenically unsaturated carboxylic monomer and 5 to 50% by weight copolymerisable ethylenically unsaturated monomer into a gaseous environment wherein solvent is removed to form the fibre or film, characterised in that the solution which is extruded contains a dissolved chemical which is retained in the fibre or film and which alters the properties of or has an effect on the fibre or film or on an aqueous fluid subsequently absorbed by the fibre or film.

11. A process according to claim 10, characterised in that the solution of the matrix copolymer is an aqueous solution containing 30 to 45% by weight of the matrix copolymer.

12. A process according to claim 10 or claim 11, characterised in that the solution is extruded through a spinneret to form fibres.

13. A process according to any of claims 10 to 12, characterised in that the dissolved chemical is capable of becoming bonded to the matrix copolymer and the fibre or film is subjected to conditions such that the chemical does become bonded to the matrix copolymer.

14. A process according to any of claims 10 to 13, characterised in that after extrusion the matrix copolymer is crosslinked.

15. A process according to claim 14, characterised in that the crosslinking, and optionally the bonding between the dissolved chemical and the matrix copolymer, is effected by heating the fibre or film at a temperature in the range 150 to 250°C.

16. A process according to claim 14 or claim 15, characterised in that the fibre or film is stretched before effecting the crosslinking of the copolymer.

17. A process for applying a controlled quantity of a chemical to a desired location, characterised in that a solution of the said chemical and a non-crosslinked copolymer of 50 to 95% by weight ethylenically unsaturated carboxylic monomer and 5 to 50% by weight copolymerisable ethylenically unsaturated monomer is extruded through a spinneret or die into a gaseous environment wherein solvent is removed to form fibre or film, and the fibre or film is applied to the desired location, optionally after crosslinking.

18. A process according to claim 17, characterised in that the fibre or film is applied to the desired location with the copolymer in its non-crosslinked state.

19. A process according to claim 17, characterised in that the copolymer is partially crosslinked or lightly crosslinked sufficiently to increase the molecular weight of the copolymer, but not sufficiently to cause the fibre or film to become water-insoluble, by treatment of the fibre or film before the fibre or film is applied to the desired location.

20. A process according to any of claims 17 to 19, in

which the solution is extruded through a spinneret to form fibres and the fibres are applied to the desired location in the form of a web of fibres.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 93/01239

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 D01F1/10; D01F1/06; A61L15/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	D01F ; A61L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
P,A	WO,A,9 219 799 (COURTAULDS PLC.) 12 November 1992 see the whole document	1-3,8-20
A	EP,A,0 436 514 (ARCO CHEMICAL TECHNOLOGY INC.) 10 July 1991 see the whole document	1-3
A	FR,A,2 383 250 (BAYER AG) 6 October 1978 see page 5, line 24 - page 7, line 6; claims	1,5
A	EP,A,0 269 393 (ALLIED COLLOIDS LIMITED) 1 June 1988 cited in the application see claims	1-3,8-20

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° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
23 JULY 1993	13.08.93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BLAS V.

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 167 (C-425)(2614) 28 May 1987 & JP,A,61 296 111 (DAICEL CHEM. IND. LTD.) 26 December 1986 see abstract ---	4
A	EP,A,0 341 951 (DOW CORNING LTD.) 15 November 1989 see the whole document -----	1,5

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9301239
SA 74985

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 23/07/93
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9219799	12-11-92	None	
EP-A-0436514	10-07-91	US-A- 5026784	25-06-91
		JP-A- 4211456	03-08-92
		US-A- 5151465	29-09-92
		US-A- 5079306	07-01-92
FR-A-2383250	06-10-78	DE-A- 2710496	14-09-78
		AT-B- 358708	25-09-80
		BE-A- 864759	11-09-78
		CA-A- 1096773	03-03-81
		GB-A- 1600103	14-10-81
		JP-A- 53139895	06-12-78
		NL-A- 7802600	12-09-78
EP-A-0269393	01-06-88	DE-A- 3782315	26-11-92
		DE-A- 3784027	18-03-93
		EP-A,B 0268498	25-05-88
		JP-A- 63159405	02-07-88
		JP-A- 63159440	02-07-88
		US-A- 4861539	29-08-89
		US-A- 4962172	09-10-90
EP-A-0341951	15-11-89	US-A- 4990338	05-02-91
		AU-B- 612832	18-07-91
		AU-A- 3405889	09-11-89
		JP-A- 2014741	18-01-90
		US-A- 4985023	15-01-91
		US-A- 5045322	03-09-91
		US-A- 5035892	30-07-91
		US-A- 5061487	29-10-91

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82